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EXPERIMENTAL PROTOCOL FOR DETERMINING HYDROXYL RADICAL REACTION RATE CONSTANTS

by

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16. ABSTRACT

An experimental protocol for the determination of rate constants for the reactions of the hydroxyl (OH) radical with chemicals in the gas phase at room temperature has been developed and is described in detail. This protocol will thus provide a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e., attack by the OH radical) of organic substances which may be emitted into the environment. The experimental technique is based upon monitoring and disappearance rates of the test compound and of a reference organic, whose OH radical reaction rate constant is accurately known, in irradiated methyl nitrite-NO-organic-air mixtures. Irradiations, employing blacklamps emitting in the actinic region, are carried out in approximately 75-liter volume cylindrical Teflon bags. The concentrations of the reactants are: methyl nitrite, zero to approximately 15 ppm; NO, approximately 5 ppm; test compound, approximately 1 ppm; reference organic, approximately 1 ppm. The test compound and reference organic are monitored by gas chromatography, NO, NO_2, and NO_x by chemiluminescence, and O_3 by chemiluminescene. Using this technique, OH radical rate constants $\geq 3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} (the range of primary interest from an atmospheric point of view) can be measured.

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The experimental technique is based upon monitoring the disappearance rates of the test compound and of a reference organic, whose OH radical reaction rate constant is accurately known, in irradiated methyl nitrite-NO-organic-air mixtures. Irradiations, employing blacklamps emitting in the actinic region, are carried out in ~75-liter volume cylindrical Teflon bags. The concentrations of the reactants are: methyl nitrite, zero to ~15 ppm; NO, ~5 ppm; test compound, ~1 ppm; reference organic, ~1 ppm. The test compound and reference organic are monitored by gas chromatography, NO, NO_2 and NO_x by chemiluminescence, and O_3 by chemiluminescence. Using this technique, OH radical rate constants $\gtrsim 3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} (the range of primary interest from an atmospheric point of view) can be measured.

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SECTION 1

INTRODUCTION AND BACKGROUND

Chemical compounds emitted into the atmosphere are removed or degraded by several pathways, these being chemical gas phase reactions or wet or dry deposition. Laboratory and environmental chamber studies have shown that for the ambient atmosphere the following gas phase removal routes are likely to be important (see, for example, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Atkinson et al. 1979, Atkinson and Lloyd 1980 and references therein):

- Photolysis, which involves absorption of light followed by isomerization or decomposition
- Reaction with ozone (O_3)
- Reaction with the hydroxyl (OH) radical
- For aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO_3) radical (Carter et al. 1981).

Hence, in order to assess (a) the atmospheric lifetime of compounds with respect to these gas-phase removal processes and (b) the relative importance of each of these reaction pathways, rate constants for photolysis and/or chemical reaction must be experimentally determined for individual compounds.

The experimental procedure detailed in this protocol is designed to enable rate constants for reaction with the OH radical to be determined at room temperature.

A. Atmospheric Hydroxyl Radical Reactions

In the atmosphere, where the reaction

$$OH + \text{chemical} \rightarrow \text{products}$$

occurs, the decay of the chemical via this reaction is given by

$$-d[\text{chemical}]/dt = k^{OH}[OH][\text{chemical}] \quad \text{(I)}$$

where [ ] denotes concentration and k^{OH} is the rate constant for reaction of the OH radical with the particular chemical. Equation (1) may be rearranged to yield

$$-d\ln[\text{chemical}]/dt = k^{OH}[OH] \quad \text{(II)}$$

and, providing the OH radical concentrations remains constant,

$$\ln([\text{chemical}]_{t_o}/[\text{chemical}]_t) = k^{OH}[OH](t-t_o) \quad \text{(III)}$$

where $[\text{chemical}]_{t_o}$ and $[\text{chemical}]_t$ are the concentrations of the chemical at times t_o and t, and ln is the logarithm to the base e. In the ambient troposphere, OH radical concentrations vary as a function of time of day, being negligibly low at night, and building up to a peak at around solar noon. However, for approximate lifetime calculations, an <u>average</u> OH radical concentration of ~8 x 10^5 molecule cm^{-3} may be assumed for the northern hemisphere (Jeong and Kaufman 1979, Kurylo et al. 1979). The assumptions inherent in these lifetime calculations must be borne in mind, especially for organics whose lifetime is of the order of one day or less. The 1/e lifetime, τ^{OH}, (i.e., the time for the concentration of the chemical due to reaction with the OH radical to decrease by a factor of e = 2.7) of any chemical with respect to reaction with the OH radical is given by

$$\tau^{OH} = (k^{OH}[OH])^{-1} \quad \text{(IV)}$$

where [OH] is the ambient atmospheric concentration (both k^{OH} and [OH] must be in compatible units (i.e., cm^3 $molecule^{-1}$ sec^{-1}, liter $mole^{-1}$ sec^{-1} or ppm^{-1} min^{-1} units for k^{OH} and molecule cm^{-3}, mole $liter^{-1}$ or ppm units, respectively, for [OH]).

For a typical troposphere OH radical concentration of 8 x 10^5 molecule cm^{-3}, the rate constants which yield 1/e lifetimes of one hour, one day, one week, one month and one year are given in Table 1 for the three sets of most commonly used units. For lifetimes longer than a day or so, the variation of temperature with altitude must be taken into account for rigorous calculations.

Table 1. Rate Constants for Reaction with the OH Radical which Yield Selected 1/e Lifetimes in the Presence of 8×10^5 molecule cm^{-3} of OH Radicals

Lifetime	Rate Constant		
	ppm^{-1} min^{-1}	liter $mole^{-1}$ sec^{-1}	cm^3 $molecule^{-1}$ sec^{-1}
1 hour	5.2×10^6	2.1×10^{11}	3.5×10^{-10}
1 day	2.1×10^4	8.8×10^9	1.5×10^{-11}
1 week	3.0×10^3	1.3×10^9	2.1×10^{-12}
1 month	7.0×10^2	2.9×10^8	4.8×10^{-13}
1 year	5.8×10^1	2.4×10^7	4.0×10^{-15}

The experimental approach described below, which is designed to provide quantitative data on both the hydroxyl radical reaction rate constants and the photolysis rate constants of organics, is based on measuring the relative disappearance rates of the test compound and of a reference organic in the presence of OH radicals. OH radicals are generated from the photolysis of varying concentrations of methyl nitrite (CH_3ONO) in air (Atkinson and Lloyd 1980):

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In the presence of added organics, the OH radicals react with these organics:

$$OH + \text{test compound} \rightarrow \text{products} \quad (1)$$

$$OH + \text{reference organic} \rightarrow \text{products} \quad (2)$$

In addition, the test compound may, in some cases, also photolyze, react with ozone and/or react with the NO_3 radical:

$$\text{test compound} + h\nu \rightarrow \text{products} \quad (3)$$

$$\text{test compound} + O_3 \rightarrow \text{products} \quad (4)$$

$$\text{test compound} + NO_3 \rightarrow \text{products} \quad (5)$$

Reactions (4) and (5) will be unimportant provided that excess NO is present since O_3 and NO_3 both react rapidly with NO:

$$NO + O_3 \rightarrow NO_2 + O2$$

$$NO + NO_3 \rightarrow 2\ NO_2$$

If the organics are lost only by reaction with OH radicals and, for the test compound, photolysis; then

$$-d[\text{test compounds}]/dt = k_1[OH][\text{test compound}] + k_3[\text{test compound}] \quad (V)$$

$$-d[\text{reference organic}]/dt = k_2\ [OH][\text{reference organic}] \quad (VI)$$

where k_1 and k_2 are the OH radical rate constants for reactions (1) and (2), respectively, and k_3 is the photolysis rate constant. Hence

$$d\ln[\text{test compound}]/dt = k_1[OH] + k_3 \quad (VII)$$

and

$$d\ln[\text{reference organic}]/dt = k_2[OH] \quad (VIII)$$

Elimination of the OH radical concentration and integration leads to

$$\frac{1}{(t-t_o)} \ln \left\{ \frac{[\text{test compound}]_{to}}{[\text{test compound}]_t} \right\} = k_3 + \frac{k_1}{k_2(t-t_o)} \ln \left\{ \frac{[\text{reference organic}]_{to}}{[\text{reference organic}]_t} \right\} \quad (IX)$$

where $[\text{test compound}]_{t_o}$, $[\text{reference organic}]_{t_o}$ are the concentrations of the test compound and the reference organic, respectively, at time t_o, and $[\text{test compound}]_t$, $[\text{reference organic}]_t$ are the corresponding concentrations at time t. Note that equation (IX) is valid even if the OH radical concentration varies with time.

Hence a plot of $(t-t_o)^{-1}\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against $(t-t_o)^{-1}\ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 and intercept k_3. Knowing k_2, the rate constant k_1 may then be derived. If the test compound does not photolyze (i.e., $k_3 = 0$), then equation (IX) can be simplified to yield:

$$\ln \left\{ \frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t} \right\} = \frac{k_1}{k_2} \ln \left\{ \frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t} \right\} \quad (X)$$

and a plot of $\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against $\ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 with a zero intercept.

The concentrations of the test compound and the reference organic are monitored before and during irradiation of the CH_3ONO/NO/test compound/reference organic/air mixtures by gas chromatography. Hence the lower limit to k_1 that can be determined is set by the precision of the gas chromatographic analyses, but is expected to be of the order of $\leq 3 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} which corresponds (Table 1) to an atmospheric lifetime of greater than one month.

SECTION 2

GENERAL EQUIPMENT AND MATERIALS REQUIRED

To determine rate constants for the reaction of OH radicals with organics using the method outlined above, the following major equipment is needed:

- Gas chromatographs for the analysis of the test and reference organics
- An ozone monitor equipped with a filter to remove particulates
- An NO-NO_2-NO_x monitor
- A Teflon bag or chamber in which the reaction can be carried out
- An arrangement of fluorescent lamps
- Gas chromatographic laboratory for precision gas phase analyses of the test and reference organics
- A greaseless high vacuum rack

The specific requirements and recommendations for these items of equipment are discussed below.

A. Methods for the Analyses of the Test and Reference Organics

While it can be seen [equations (IX) and (X)] that only relative measurements of the test and reference organic concentration are necessary, it is recommended that quantitative analyses be carried out. For the development of this experimental protocol, gas chromatography has been used to analyze the test and reference organics. However, any analysis technique that is specific for the test and reference organics and which samples over a time period short compared to the irradiation times can in principle be used (e.g., mass spectrometry, combined gas chromatography-mass spectrometry and spectroscopic techniques). Since sampling for the test and reference organics must be carried out simultaneously for this protocol, the same technique of choice must be used in both cases. It is taken for granted that quantitative analyses of the test compound by such techniques (at the concentrations necessary for this protocol, i.e., ~0.1-1 ppm) will have been developed by the chemical manufacturer. Hence, this aspect of the protocol is considered beyond the scope of this document.

For the reference organics which are recommended for use here (see Section 3F), the gas chromatographic columns and conditions used in the development of this protocol were as follows (Pitts et al. 1979):

n-Butane, cyclohexane, isoprene, 2-methyl-2-butene and methyl nitrate (and other C_4 through C_{10} n-alkanes) were analyzed using a 20 ft x 1/8 in stainless steel column with 5% DC703/C20M on 100/120 mesh AW, DMCS Chromosorb 6, operated at 333 K. The N_2 carrier gas flow was 50 cm^3 min^{-1}, and a 3.0 cm^3 gas sample loop was used.

Propene, n-butane (and other > C_3 alkanes and alkenes) were analyzed using a 36 ft x 1/8 in stainless steel column of 10% 2,4-dimethylsulfolane (DMS) on C-22 firebrick (100/120 mesh) operated at 273 K. The N_2 carrier gas flow was 80 cm^3 min^{-1} and a 2.0 cm^3 gas sampling loop was used.

For all of these analytical systems, no preconcentration was necessary and flame ionization was employed in all uses.

It is recommended that these or equivalent gas chromatographic analysis techniques be used for methyl nitrite and the reference organics given in Section 3F.

B. Ozone Monitor

A chemiluminescence ozone analyzer is recommended for this protocol since the ozone analyzers utilizing ultraviolet absorption tend to respond not only to ozone but also to some chemicals which absorb radiation at 253.7 nm (e.g., the cresols [Atkinson et al. 1980]). This may include some of the OH radical reaction products. In view of these potential problems, it is desirable to use a chemiluminescence O_3 monitor which utilizes the emission arising from the ozone-ethene reaction. The ozone analyzer used will have an optimum sampling rate specified by the manufacturer; any sampling rate less than ~2 liters min^{-1} is acceptable.

The ozone analyzer should be calibrated according to the manufacturer's specifications.

C. $NO-NO_2-NO_x$ Monitor

A chemiluminescence $NO-NO_2-NO_x$ monitor (using the ozone-nitric oxide reaction) is recommended for this protocol. The monitor should be calibrated according to the manufacturer's specifications.

D. Reaction Chamber and Fluorescent Lamp Irradiation Assembly

1. Reaction Chamber

A simple, yet totally adequate, reaction chamber consists of an ~75-liter FEP Teflon cylindrical reaction bag (FEP Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.), formed from three pieces of 2 mil FEP Teflon (Figure 1). The two endpieces are ~45 cm in diameter with an ~45 cm wide, ~140 cm long piece forming the cylinder. Teflon is the preferred material for construction of the reaction chamber because of its general inertness to ozone and its lack of hydrocarbon offgassing.

2. Injection and Sampling Port

Prior to heat sealing the Teflon chamber sides, a port for injection of the reactants and for sampling must be fitted. This sampling and injection port should be constructed of TFE Teflon (TFE Teflon is a registered trade name of E I. du Pont de Nemours and Co., Inc.) nuts and bolts with the appropriate Swagelok (Swagelok is a registered trade name of Crawford Fitting Company) stainless steel fittings.

Figure 2 shows the design of the sampling and injection port used in developing this protocol. The port consists of a 2-3" long hollow bolt of Teflon (A), machined on the exterior surface with threads. The interior hole (B) is 1/4" in diameter and an ~8" long 1/4" o.d. Teflon tube is inserted as shown. Two Teflon nuts (D) then screw over the bolt (A), one on the inside of the bag, the other on the outside. Large Teflon washers (E) are placed between the Teflon bag and the nuts (D), thus enabling the nuts to be tightened without twisting or stretching the Teflon bag. The 1/4" o.d. Teflon tube is connected outside the reaction bag to a glass-Teflon stopcock.

3. Heat Sealing

The Teflon port is first assembled on one of the ends of the chamber by tightening the Teflon nuts, as detailed above and as shown in Figures 1 and 2. The hole in the Teflon sheet through which the Teflon bolt (A) fits can be conveniently made using a cork borer. The sides of the resulting cylindrical bag are sealed together with a 500 watt thermal impulse heat sealer. It will probably be necessary to carry out preliminary testing of this heat sealing technique using scrap pieces of Teflon to obtain a heat setting that yields a strong seal.

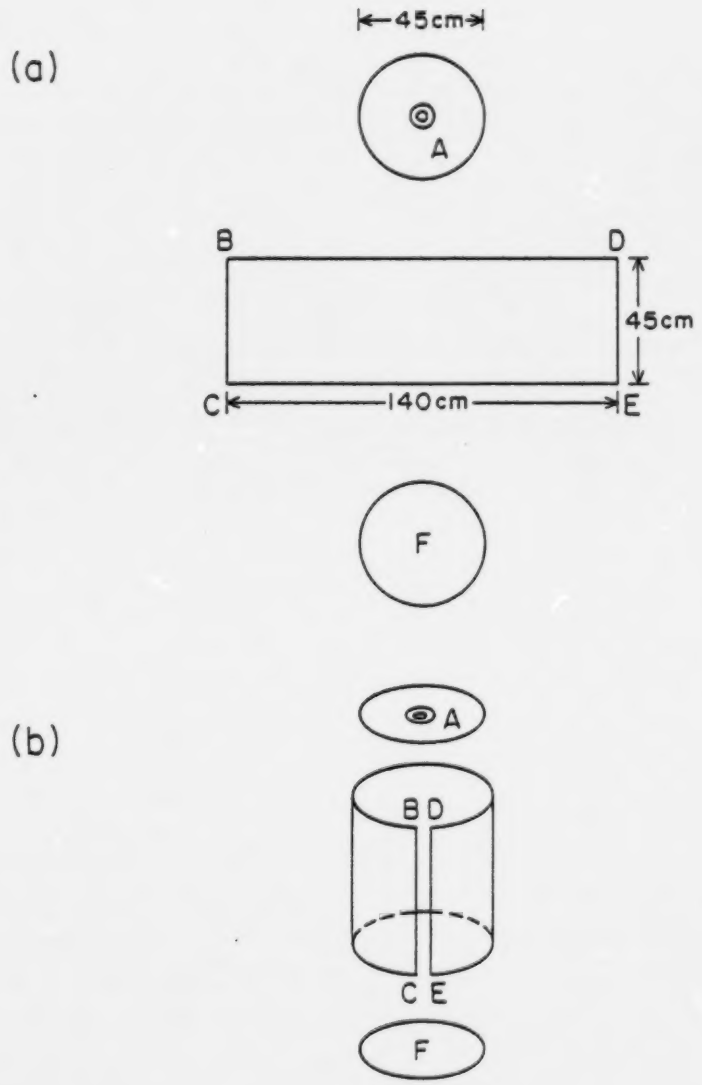
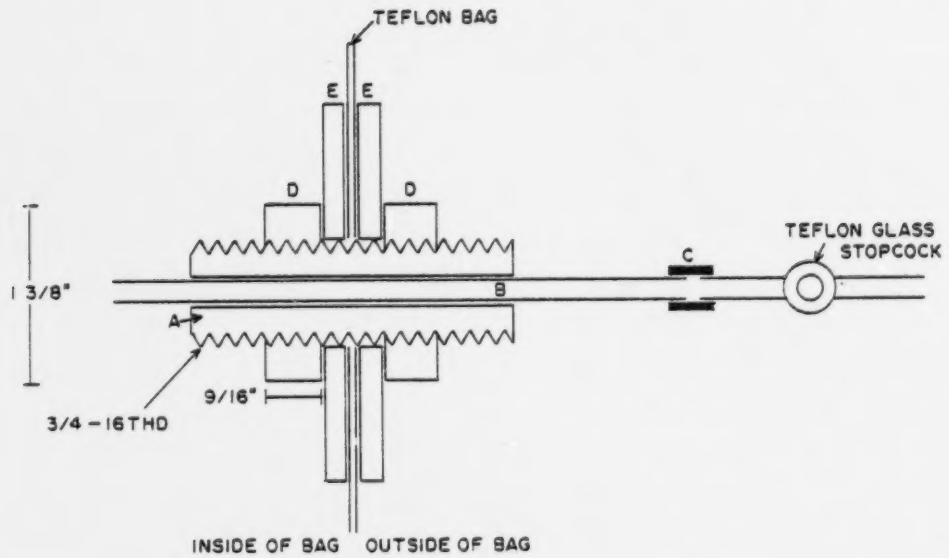


Figure 1. Construction of the Teflon Reaction Bag



A HOLLOW TEFLON BOLT
B 1/4" O.D. TEFLON TUBE INSERTED THROUGH 1/4" DIAMETER HOLE
C TYGON TUBING
D TEFLON NUTS
E TEFLON WASHERS

Figure 2. Injection and Sampling Port

E. Reaction Bag Cover

An opaque cover is necessary in order to avoid illumination of the chamber and hence possible photolysis of the methyl nitrite or the test compound being studied. A large opaque plastic sheet functions well.

F. Seal Reinforcement and Leak Testing

The heat sealed sides can be further protected from leaks by covering the heat-sealed seams with green Mylar tape. After the bag is constructed it should be tested for obvious leakage by filling with pure air (ultra-high purity) to capacity (not excessively so as to split the seams) and then allowing the inflated bag, with the stopcock closed, to sit for one or two hours. After this period of time, the amount of deflation can be visually estimated. A certain amount of air will have permeated through the Teflon, but the bag should still be largely filled, and no obvious leaks should result from applying a small amount of pressure to the bag. The seams should be carefully examined for splits or tears, and, if any are found, they should be resealed (probably at a lower heat setting) and more Mylar tape applied to reinforce the seams.

G. Fluorescent Lamp Assembly

The fluorescent lamp assembly used in the development of this protocol is shown schematically in Figure 3. It consists of a circular array of 24 15-watt blacklights (GE F15T8-BL15) mounted in a cylindrical frame constructed out of aluminum. The lamps are arranged on three electrical circuits, eight lamps per circuit, with every third lamp being on a given circuit. This allows the use of three differing light intensities. In the bottom of the chamber is a fan which circulates a large volume of air to minimize the amount of heating. A cylindrical wire mesh screen inside of the lamp assembly in which the Teflon bag is placed (Figure 3) keeps the reaction bag from contact with the lamps or the fan.

H. Vacuum Gas-Handling System

A suitable gas-handling system is shown diagramatically in Figure 4. Such a system should preferably be constructed from Pyrex, since the use

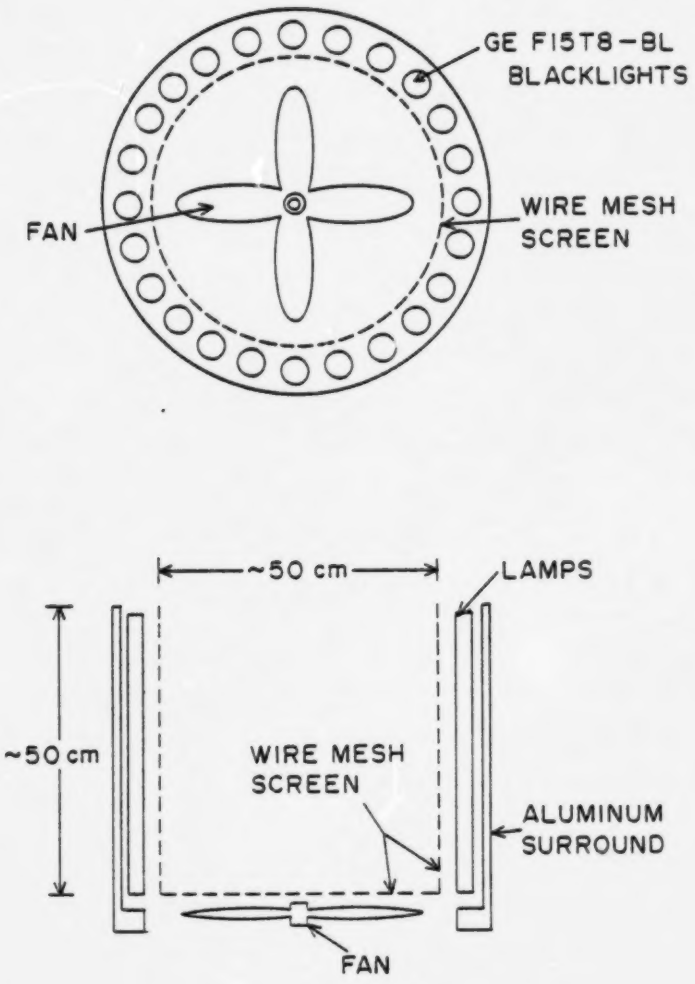
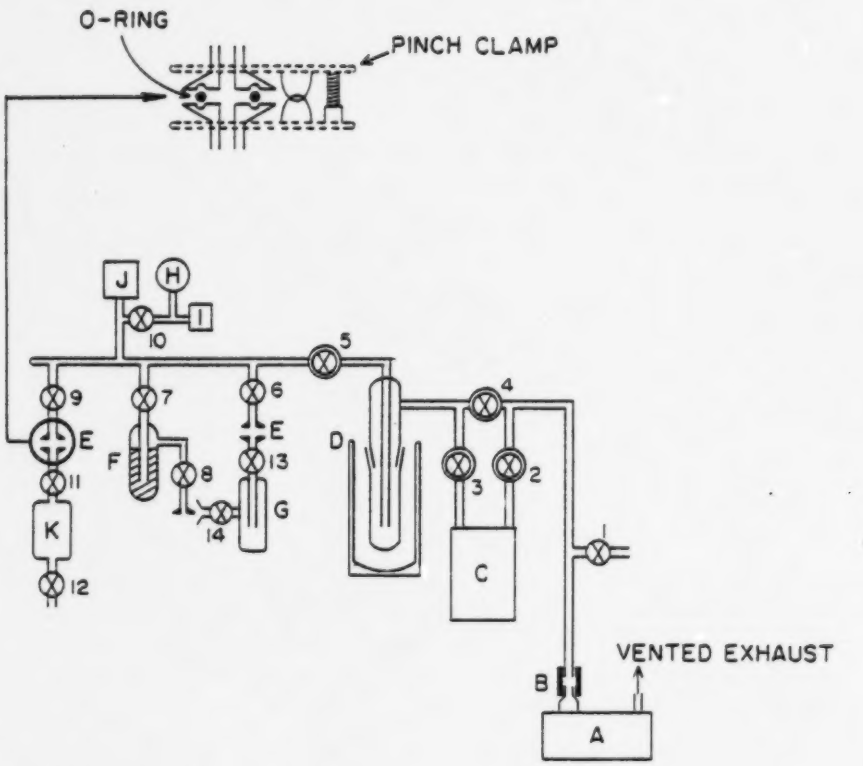


Figure 3. Fluorescent Lamp Assembly



A ROTARY PUMP
B RUBBER TUBING (THICK WALLED)
C DIFFUSION PUMP
D TRAP AT LIQUID NITROGEN TEMPERATURE
E #7 OR 9 O-RING JOINTS
F MOLECULAR SIEVE 4A TRAP
G CH_3ONO TRAP
H THERMOCOUPLE GAUGE
I IONIZATION GAUGE
J CAPACITANCE MANOMETER
K ~500cm^3 PYREX BULB

⊗ 0-4 OR 0-5 mm STOPCOCKS

⊗ 0-8 OR 0-10 mm STOPCOCKS

Figure 4. Schematic of Gas Handling Vacuum Rack

of other materials, such as various metals, can lead to wall adsorption problems. The components of such a gas handling system are discussed below.

1. Vacuum Pumping System

Two pumps, working in tandem, are necesary to provide good vacuum, i.e., pressures $\lesssim 10^{-5}$ torr. The forepump (A) must be capable of achieving pressures $\lesssim 0.05$ torr. A rotary pump such as a Welch Model 1402 Duo-Seal or equivalent is recommended for this purpose. The forepump is attached to the rest of the vacuum system by heavy-walled rubber vacuum tubing (B), which also serves to damp-out transmission of vibrations to the vacuum line. The exhaust from this pump should be vented into a hood. The second, and high-vacuum, pump required is a multistage oil diffusion pump (C), a CVC (Consolidated Vacuum Corporation) VMF-10 or VMF-20 or equivalent being suitable. The working fluid should be a silicone oil (e.g., Dow-Corning D.C. 703) since they are less susceptible to destructive oxidation should the system be inadvertently vented to air while the diffusion pump is still hot. The diffusion pump fluid must have a room temperature vapor pressure of $\lesssim 10^{-6}$ torr.

The pumping system must be equipped with a trap (D) cooled by liquid nitrogen (i.e., at 77°K) to reduce pump oil contamination and back-streaming. The cone and socket portions of this trap (Figure 4) may be conveniently sealed using Apiezon W wax (which requires gentle heating to apply).

2. Vacuum Rack

A suitable assembly of the vacuum rack is as shown in Figure 4. The stopcocks should be of Teflon with Viton "o"-rings, such as the Kontes #K-826500 or K-826510 series. The "o"-ring joints (#7 or #9 size are suitable) must be chosen to be compatible with those on the gas absorption cell. These "o"-ring joints should be clamped by pinch clamps with a screw lock device (Thomas #18A, available from VWR Scientific, Inc., for example).

3. Pressure Gauges

Two, or preferably three, pressure gauges are required:

(a) An ionization gauge to measure high vacuum, i.e., pressures $\lesssim 10^{-3}$ torr, to verify that the vacuum system is operating correctly and that there are no leaks.

(b) If available, a thermocouple gauge is desirable to monitor, on a semi-quantitative basis, pressures in the range ~10^{-3} to 1 torr. This gauge is used to monitor the pressures in the gas handling system prior to turning on either the diffusion pump (which requires pressures of $\lesssim$ 0.1 torr) or the ionization gauge. A convenient and totally satisfactory pressure monitoring system which includes both these gauges is the CVC Products, Inc. Model GIC-300A ionization gauge with associated thermocouples, or equivalent.

(c) The third pressure gauge is needed to accurately monitor pressures of the test compound and diluent in the range ~0.01 to 760 torr. It is recommended that for this purpose a capacitance manometer be used, such as an MKS Baratron 310 BHS-1000 with an associated 170-6C electronics unit and a digital readout (this particular system has an accurately useable range of < 0.1 to 1000 torr). While these vacuum gauges exhibit a slow zero drift, they can be readily rezeroed using the ionization gauge, i.e., when the ionization gauge reads $\lesssim 10^{-3}$ torr.

I. Glassware for Preparation of Methyl Nitrite

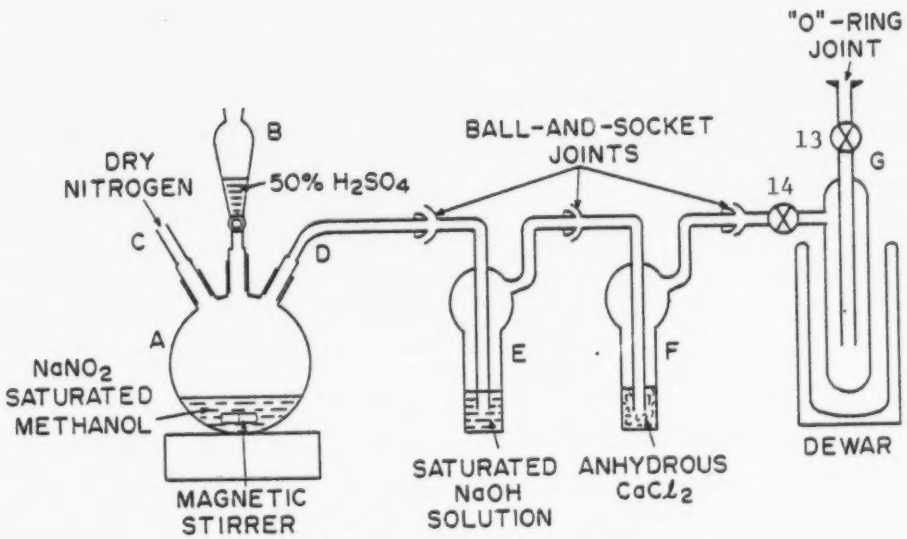
The glassware required for the preparation of methyl nitrite is as follows and is shown in Figure 5:

- A 300 ml three-necked flask
- A 250 ml separating funnel with an appropriate ground glass joint
- Two bubblers fitted with the appropriate 12/5 ball and socket joints
- A Pyrex trap fitted with high vacuum greaseless Teflon stopcocks, and the appropriate ball and socket joint and "o" ring joint (Figure 5).
- Other associated glass fittings as shown in Figure 5.

J. Flowmeter

1. Range and Application

A rotameter (Matheson 604 flowmeter or its equivalent) with a flow range of ~1 to 10 liter min^{-1} is an effective means for controlling and monitoring the rate of fill of the reaction chamber. When not flushing a test compound into the chamber, the fill rate may be relatively rapid, i.e., ~7-10 liter min^{-1}. However, when a liquid needs to be introduced into the chamber, this is accomplished by flushing an ~1-liter bulb containing the compound of



A 300ml THREE-NECKED ROUND BOTTOMED FLASK

B 250ml SEPATORY FUNNEL

C DRY NITROGEN INLET

D NITROGEN-CH_3ONO OUTLET

E,F BUBBLERS

G TRAP

⊗ HIGH-VACUUM GREASE-LESS STOPCOCKS (0-4 OR 0-5mm)

◎ TEFLON STOPCOCK

Figure 5. Schematic of Glassware Assembly for Methyl Nitrite Production

interest with pure air into the bag at a lower flow rate, i.e., ~3 liter min^{-1} (at high flow rates the test compound may not fully vaporize before the bag is filled). A slower flow rate still may be useful for particularly nonvolatile compounds, though use of a heat gun will aid vaporization in these cases.

2. Calibration of the Rotameter

Rotameters are often accompanied by a manufacturer's calibration curve for air. Although this calibration curve, if available, could be used, it is advisable to determine accurately the flow rate calibration curve. Flow rates should be determined at several (at least five) rotameter settings covering the flow rates to be used (i.e., 1-10 liter min^{-1}). At these flow rates a wet test meter (Precision Scientific Model No. 63126 or equivalent) is preferable, although a 1000 cm^3 or (preferably) a 2000 cm^3 bubble flowmeter can also be used. If neither a wet test meter nor a bubble flowmeter is available, a bubble flowmeter can be readily constructed by narrowing one end of a large glass tube (~5 cm diameter), as shown in Figure 6.

Indelible lines can be drawn on the glass at intervals of 100 cm^3 by adding water from a 100 cm^3 volumetric flask which has been filled to the mark and noting the water level after each successive addition of water (with, as shown in Figure 6, the zero line being above the narrow portion of the flowmeter), with the flowmeter in a vertical position. To the narrow end of the glass tube a glass "T" is attached by Tygon tubing, and the lower arm is enclosed with a disposable pipette bulb. A Tygon tubing line which carries the gas is attached to the other arm of the "T".

The pure air should first be sent through the rotameter, and its setting adjusted and noted. When using a wet test meter, measure the time, t, for a change of volume, V. For a bubble flowmeter, first squeeze the pipette bulb (containing soap solution, e.g., SNOOP [a registered trade name of Nupro Company]) to start a soap bubble and again measure the time, t, for the soap bubble to pass through a known volume V (the sidewalls of the bubble flowmeter should be well washed with soap solution so that bubbles will not break). For both types of flowmeters at least three repeat readings should be taken at each rotameter setting. The volumes V

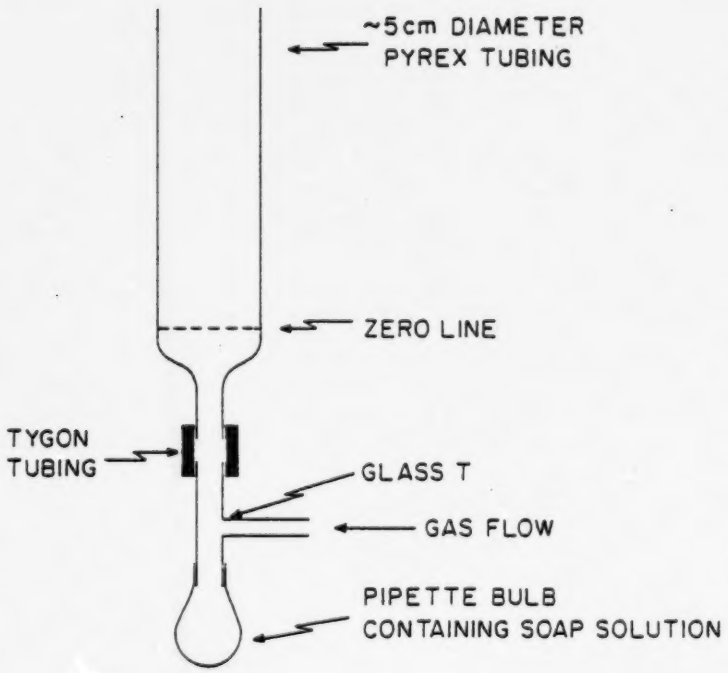


Figure 6. Design of a Bubble Flowmeter

should be such that the corresponding times t exceed 10 seconds. The flow rate F (in liter min^{-1}) is given by

$$F = \frac{V(cm^3) \times 60}{t(sec) \times 1000} \qquad (XI)$$

K. Temperature Measurement

A thermometer or thermocouple suitable for measuring the temperature in the immediate vicinity of the reaction bag is required. A simple thermometer covering the range 0 to 100°C, with an accuracy of $\pm$ 0.1°C is eminently suitable.

SECTION 3

EXPERIMENTAL PROTOCOL

A. Operation of Gas Handling System

1. Start-Up

The following describes briefly the typical start-up operation of the vacuum gas handling system (Figure 4) as regards this protocol.

(1) With all stopcocks closed, switch on rotary pump (A), then open stopcock 4 and place a Dewar of liquid nitrogen around trap D.

(2) Open stopcock 10 and monitor the pressure using the thermocouple gauge (H). If the pressure is > 0.1 torr, then open stopcock 5. When the pressure as read by the thermocouple gauge (H) is < 0.1 torr, turn on the diffusion pump (C), open stopcocks 2 and 3 and close 4. When the diffusion pump has reached operating temperature, the pressure in the vacuum manifold should be < 10^{-5} torr as read by the ionization gauge (I). At this point the capacitance manometer (J) can be zeroed. The ionization gauge (I) should only be used when, as indicated by the thermocouple gauge (H), the pressure is $\leq 10^{-3}$ torr.

(3) The ~500 ml Pyrex bulb cell (K) can now be evacuated by opening stopcocks 9 and 11. If the bulb is at a substantial pressure, then prior to opening these stopcocks, the diffusion pump should not, if possible, be exposed to pressures > 0.1 torr to avoid degradation of the pump oil. It should be pointed out that it is good practice after the experiments have been completed to evacuate the bulb (K) prior to shutting down the gas handling system.

2. Shut-Down

The gas-handling system can be shut down by the following procedure: (a) close stopcocks 5 to 11, (b) switch off the diffusion pump, (c) when the diffusion pump is cool, close stopcocks 2 and 3 and open 4, (d) remove the Dewar from trap (D) and allow it to warm up, (e) then close stopcock 4 and switch off the rotary pump, thus preventing back-up of the rotary pump oil. With this procedure, the vacuum manifold, the trap (D) and the diffusion pump are left under vacuum.

3. Maintenance

If the vacuum system, including the bulb (K) (i.e., all stopcocks open except stopcocks 1, 4, 6 and 7) does not pump down to < 10^{-4} torr, then either a leak or contaminant offgassing problems are present. Closing stopcocks 11, then 9, will give indications as to the region of the problem i.e., if, on closing stopcock 9 the pressure drops, then there may be a leak around the "o"-ring joint on the ~500 ml bulb (K), which then should be replaced. If, however, the pressure drops on closing stopcock 11 (with 9 open) then either the bulb has a leak, or offgassing from previous runs is occurring. Leaks can be checked using a Tesla coil. Such "maintenance" procedures should be routinely carried out on all portions of the vacuum gas handling system. This includes changing the rotary pump oil at frequent intervals.

B. Preparation of Methyl Nitrite

Methyl nitrite (CH_3ONO) is prepared by the dropwise addition of 50% H_2SO_4 to a sodium nitrite ($NaNO_2$) saturated solution of methanol (CH_3OH). For the protocol described here, the use of ~50 cm^3 of each (50% H_2SO_4 and sodium nitrite saturated methanol) is sufficient. A schematic of the apparatus needed is shown in Figure 5. A solution of methanol saturated with sodium nitrite is placed in the three-necked flask (300 ml volume) (A). The 50% H_2SO_4 is placed in the funnel (B) equipped with a Teflon stopcock. Ultra-high purity nitrogen is flowed through the flask via inlet and outlet joints (C) and (D). Bubblers (E) and (F) contain a saturated NaOH solution and anhydrous $CaCl_2$, respectively, while trap (G) is fitted with high vacuum greaseless stopcocks (Kontes #K-826500 or equivalent) and the necessary ball and socket joints and "o"-ring, as shown. The system should be purged with a nitrogen flow for ~10 minutes prior to commencing the dropwise addition of H_2SO_4 into the $NaNO_2$ saturated CH_3OH. The trap (G) should be cooled to 196 K by means of a Dewar filled with a dry ice/acetone slush just prior to beginning the reaction. The CH_3ONO produced is swept out of the reaction vessel by the N_2 stream, any H_2SO_4 carried over is removed by passage through the NaOH solution, and the CH_3ONO-N_2 stream is then dried by passage

through the trap containing anhydrous $CaCl_2$. The CH_3ONO is collected in the cold trap (G).

After the reaction has terminated, the N_2 flow is turned off, stopcocks 13 and 14 on the trap (G) are closed, and the trap, still cooled to dry ice/acetone temperature by the Dewar, is connected to the vacuum system (Figure 4) via the "o"-ring joint (E). The Dewar containing dry ice/acetone is then replaced by a Dewar containing liquid nitrogen.

After preparation of the methyl nitrite, as described above, the trap (G) is degassed by opening stopcocks 6 and 13, with the trap still cooled to liquid nitrogen temperature. After pumping down to $< 10^{-4}$ torr, stopcock 13 is closed, and the methyl nitrite can be stored indefinitely at liquid nitrogen temperatures under vacuum. The trap (G) and Dewar should, if possible, be covered with an opaque cover (e.g., aluminum foil) in order to avoid any photolysis of the methyl nitrite.

C. Experimental Procedure for the Determination of Rate Constants for Reaction with the Hydroxyl Radical

1. Filling the Reaction Bag

Prior to each new experiment, the reaction bag should be completely emptied using a metal bellows pump whose exhaust is expelled into a hood. The bag should then be filled with pure air and pumped out again to remove any test compound or other reactants or products from the previous run. The desired amounts of the reactants (i.e., methyl nitrite, NO, the test compound and the reference organic) are then introduced (see below, Section IIIC2), and the reaction bag is filled (i.e., visually filled but not excesively so as to cause undue stress on the seams) with ultra-zero air, using a flow rate in the range of ~7-10 liter min^{-1}, as monitored by the rotameter (Liquid Carbonic, < 0.1 ppm hydrocarbons).

2. Introduction of Initial Reactants

(a) Methyl Nitrite

A convenient method of introducing CH_3ONO is to admit the desired pressure of CH_3ONO from the trap (G) into the ~500 cm^3 Pyrex bulb (K) by gradually warming the trap until the desired pressure is attained. The volume of bulb (K) should be accurately measured by, for example, the volume of water it holds. For a 500 cm^3 bulb and a 75-liter

reaction bag, 1.14 torr in the 500 cm^3 bulb corresponds to 10 ppm (at 760 torr atmospheric pressure) in the reaction bag.

The bulb (K) is first pumped down to $\leq 10^{-4}$ torr, then with stopcocks 5, 7 and 10 closed and stopcocks 6, 9, 11 and 13 open, the liquid nitrogen Dewar removed from trap (G), and the pressure is allowed to rise to the desired level, as read by the capacitance manometer (J). Stopcock 13 is then closed, the liquid nitrogen Dewar replaced around trap (G), and, after allowing the pressure to equilibrate, the pressure is read and stopcocks 11 and 9 are closed. The bulb (K) is then attached to the reaction bag as shown in Figure 7, stopcock 12 is opened, allowing air from the reaction bag to fill bulb (K), then stopcock 11 is opened and the contents of bulb (K) flushed into the reaction bag by a monitored flow of ultra-zero air.

(b) Injection of Test Compound and Reference Organic

Concentrations of the test compound and reference organic used in the development of this protocol have been in the range of 0.5 to 2 ppm by volume. The following protocol details the introduction of a compound to yield a concentration of ~1 ppm in the reaction bag.

1. Gaseous Compounds

If the test compound or reference organic is gaseous at room temperature, then the volume, V, of gaseous test compound needed is then given by:

$$V(cm^3) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{volume of reaction bag (liters)}] \quad \text{(XII)}$$

Using the reaction bag described in this protocol, approximately 0.075 cm^3 of gas are required to yield a concentration of 1 ppm in the bag. To obtain such a small volume of gas, 7.5 ml of gas is first transferred from a 10 ml all-glass gas syringe into a 100 ml all-glass gas syringe containing ~92.5 ml of pure air. For this transfer the two syringes are connected tip-to-tip by an ~0.4 in. long Tygon tube, as shown in Figure 8. The syringes are pumped back and forth a few times to ensure mixing. From this 100 ml syringe, 1.00 ml is then taken in the 10 ml syringe and injected into an ~1-liter bulb modified as shown (Figure 9), which has been pre-flushed with pure air for $\geq$ 5 minutes. The contents of this closed 1-liter bulb are then flushed into the reaction bag with pure air.

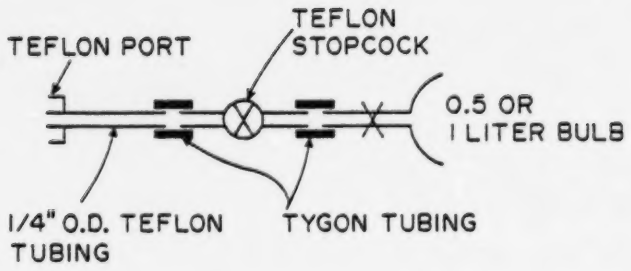


Figure 7. Attachment of Pyrex Bulbs to the Injection Port

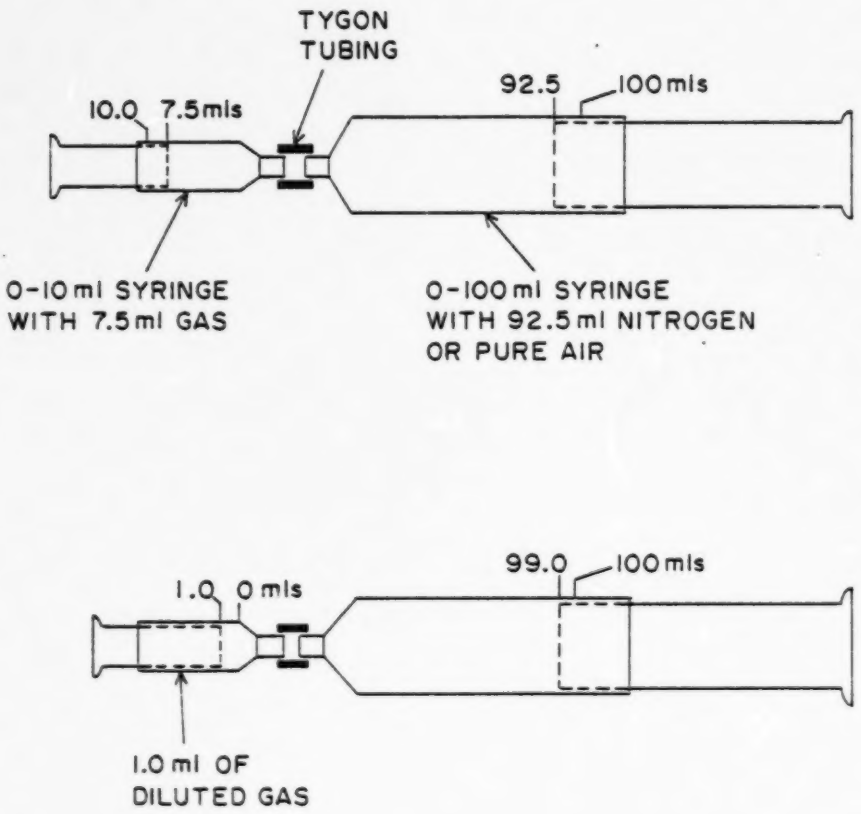


Figure 8. Syringe-to-Syringe Gas Transfer

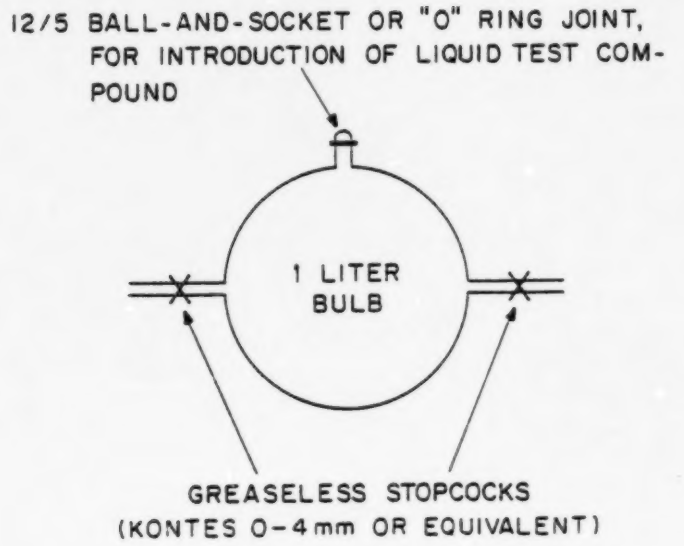


Figure 9. Design of Pyrex Bulb for Injection of Gaseous or Liquid Compounds

2. Liquid Compounds

If the test compound or reference organic is a liquid, a different method of injection and of calculating the amount needed is necessary. For the reaction bag described in this protocol approximately 0.5 μl of liquid will give a concentration appropriate for an experiment aimed at an initial concentration of ~1 ppm, since for the liquid case:

$$V\ (\mu\text{liters}) = 10^{-4} \times [\text{desired concentration (ppm)}] \times \frac{[\text{Volume of bag (liters)}] \times \text{Molecular Weight (gm)}}{\text{Density (gm cm}^{-3}) \times 2.46} \qquad \text{(XIII)}$$

at room temperature.

It is necessary that the test compound be of the highest purity possible, since if an impurity reacts with OH radicals much faster than the actual test compound, it could lead to an erroneously high rate constant and atmospheric reactivity ascribed to the test compound. For example, the presence of alkene impurities may be present in a saturated hydrocarbon. Hence, the purity of the test compound must be known, and the impurities quantitatively identified by, for example, gas chromatographic analysis.

Furthermore, any tendency of a compound to air-oxidize or polymerize will lead to low volatility residues and result in errors when carrying out liquid injections. The compounds should, if such problems are known to be likely, be distilled by conventional means, i.e., vacuum distillation with liquid nitrogen trapping, vapor transfer from trap-to-trap at dry ice temperature, or by distillation at atmospheric or subatmospheric pressure.

Full safety precautions consistent with the known or unknown toxic, mutagenic or carcinogenic hazards of the test compounds must be taken For example, if the test compound is known to be hazardous or toxic, or if there is a reason to believe that it is, then handling should be carried out in a hood with disposable gloves, using a micropipette with disposable tips. Used gloves and tips should be disposed of according to safety regulations. If the toxicity of the compound is not a problem, a 10 μl capacity Hamilton liquid syringe may be used. It should be cleaned

immediately after use by alternately drawing in and expelling methanol or some other appropriate solvent five to ten times and then completely drying it by flowing dry nitrogen or pure air through the body of the syringe.

The calculated (see equation XIII above) amount of the liquid test compound is then injected into a 1-liter bulb, modified as shown in Figure 9, which has been preflushed with pure air into the hood for $\geq$ 5 minutes. The contents of the dosed 1-liter bulb are then flushed into the bag with pure air at a known flow rate, which should be ~3.5 liter min^{-1} for a more volatile liquid or less (~1-2 liter min^{-1}) for a nonvolatile liquid. Evaporation of the lower volatility liquids may be aided by gentle use of a heat gun to warm the 1-liter bulb, taking care not to pyrolyze the test compound.

(c) Injection of NO

Injection of NO is carried out in a manner similar to that for gaseous test compounds or reference organics, except that five times as much are needed for 5 ppm, and that nitrogen is used instead of pure air in the syringes and ~1-liter bulb, to avoid oxidation to NO_2.

The reaction bag must be kept in the dark during these injections, since CH_3ONO photolyzes rapidly.

D. Experimental Procedure

When the reactants have been injected in the reaction bag and mixed, the concentrations of the test compound and the reference organic are determined by gas chromatography. Samples are conveniently taken by a 100-ml all-glass, gas-tight syringe. The syringe is flushed by withdrawing and expelling 100 ml of the gas to be sampled two or three times prior to taking the sample for analysis. While the data analysis does not require absolute concentrations, but only relative concentrations [equations (IX) and (X), Section I), the gas chromatograph(s) should preferably be calibrated for both the test compound and reference organic over the concentration range ~0.1 to ~2 ppm. A minimum of three gas chromatographic samples should be analyzed prior to turning on the lamps. If the first two analyses agree to within $\pm$ 2%, then immediately after the third sample is taken from the reaction bag, the lamp can be turned on. If the first two analyses disagree by more than 2%, then further samples should be taken until duplicate analyses do agree to within 2%.

In between gas chromatographic sampling, the $NO-NO_2-NO_x$ and O_3 monitors should be sampling from the reaction bag, and their outputs displayed on stripchart recorders. Before beginning monitoring from the bag, these analyzers should be allowed to warm up according to the manufacturer's specifications. Teflon sampling lines (1/4 in. o.d.) should be used between the bag and the O_3 and $NO-NO_2-NO_x$ monitors in order to avoid losses experienced with, for example, Tygon or nylon tubing. The first three to five minutes sampling should be neglected since initial flushing of the sample lines is needed.

When stable gas chromatographic readings have been established (see below), the desired number of lamps are turned on, together with the cooling fan. The temperature beside the reaction bag should be monitored during the irradiation. Gas chromatographic samples are taken as often as possible. This is, of course, constrained by the retention times of the test compound and of the reference organic. O_3 and $NO-NO_2-NO_x$ monitoring should be carried out between sampling. Sampling for gas chromatographic analysis of the test compound and the reference organic must be carried out simultaneously.

With the protocol developed here, the irradiation should be terminated, and the last gas chromatographic samples taken after ~30 minutes for full light intensity, ~45 minutes for two-thirds maximum light intensity or ~60-90 minutes for one-third maximum light intensity. Since it is preferable to have two to four gas chromatographic analyses during the irradiation, the optimum light intensity is then determined by the gas chromatographic retention times. As an example, Figure 10 shows a typical set of gas chromatograms for an n-butane + propene system, for which sampling periods of 15 minutes were employed.

For organics which react with ozone (i.e., the alkenes) care should be taken not to obtain data when the reaction with O_3 becomes important (i.e., > 10% of the OH radical reaction rate). The O_3 reaction rate constant k^{O_3} should have been previously measured, using the protocol described by Pitts et al. (1981a). The average OH radical concentration during a given irradiation period (times t_1 to t_2) can be determined from the rate of decay of the reference organic using equation (XIV):

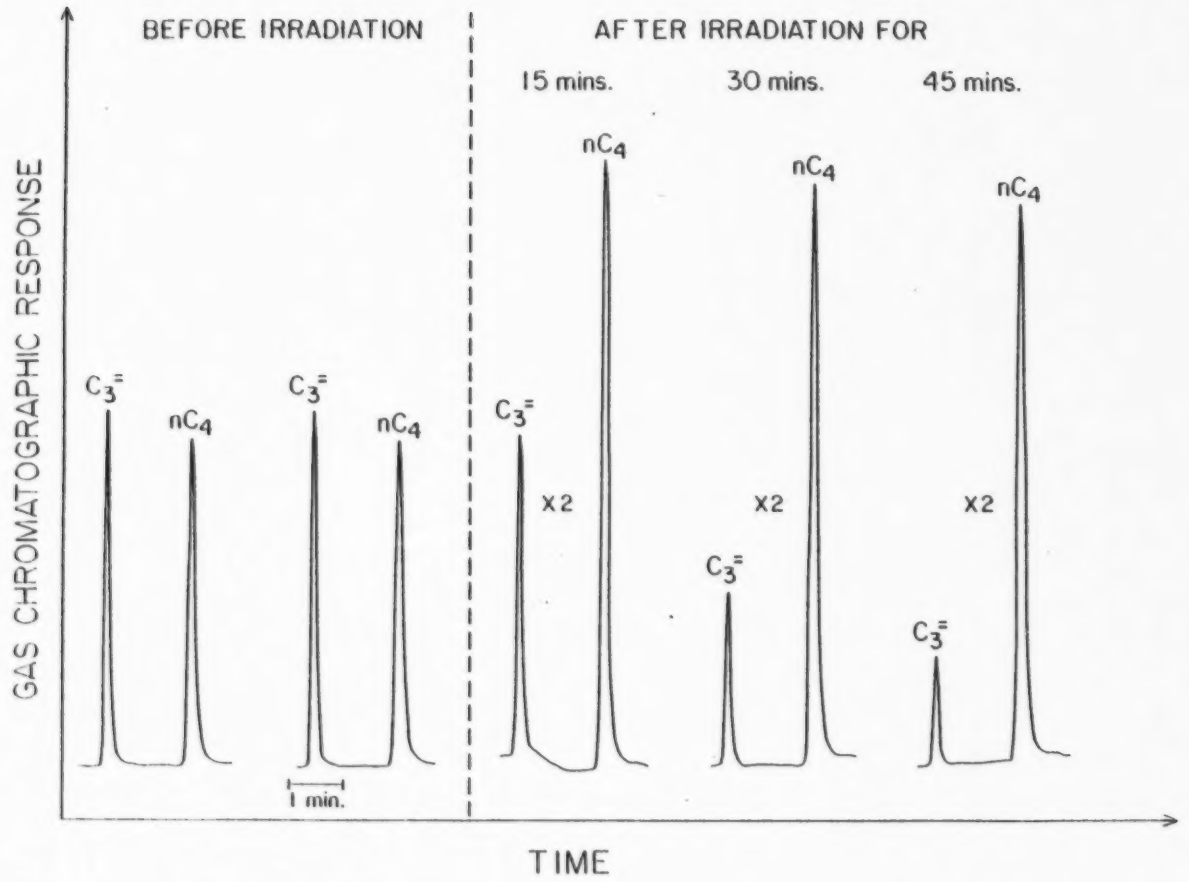


Figure 10. Example of Gas Chromatographic Analysis of Propene ($C_3^=$) and n-Butane (n-C_4) during a CH_3ONO/NO/Propene/n-Butane/Air Irradiation

$$[OH]_{avg} = \frac{\ln([\text{reference organic}]_{t_1}/[\text{reference organic}]_{t_2})}{k_2\,(t_2-t_1)} \qquad \text{(XIV)}$$

where k_2 is the rate constant for the reaction of OH radicals with the reference organics (reaction 2). The OH radical concentrations so determined during a typical irradiation, carried out at full light intensity with 10 ppm initial concentration of CH_3ONO, are shown in Figure 11. The relative importance of the O_3 reaction can be readily calculated from the O_3 and OH radical concentrations and the OH radical and O_3 reaction rate constants:

$$\text{Ratio of } O_3 \text{ reaction to OH radical reaction} = k^{O_3}[O_3]/k^{OH}[OH] \qquad \text{(XV)}$$

A value of $k^{OH} \sim 10^{-11}$ cm^3 molecule^{-1} sec^{-1} can be assumed as a first estimate. As an example, for 2.4×10^7 OH radicals cm^{-3} (Figure 11) and $k^{OH} = 1 \times 10^{-11}$ cm^{-3} molecule^{-1} sec^{-1}, then the maximum O_3 concentrations for the O_3 reaction to contribute less than 10% of the hydroxyl radical reaction for the various listed values of k^{O_3} are given in Table 2.

For reactants which react rapidly with OH radicals, the irradiations should be carried out with one-third light intensity and low (~4 ppm) concentrations of CH_3ONO, with short irradiation times ($\lesssim$ 5 minutes). For organics which exhibit an absorption spectrum in the actinic region with a significant value of the maximum photolysis rate constant (Pitts et al. 1981b), at least

Table 2. Maximum O_3 Concentrations for < 10% O_3 Reaction for Various Values of k^{O_3} (for $k^{OH} = 1 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1} and [OH] = 2.4×10^7 molecule cm^{-3})

k^{O_3} (cm^3 molecule^{-1} sec^{-1})	O_3 Concentration (ppm)
1×10^{-19}	< 10
1×10^{-18}	< 1
1×10^{-17}	< 0.1
1×10^{-16}	< 0.01
1×10^{-15}	< 0.001

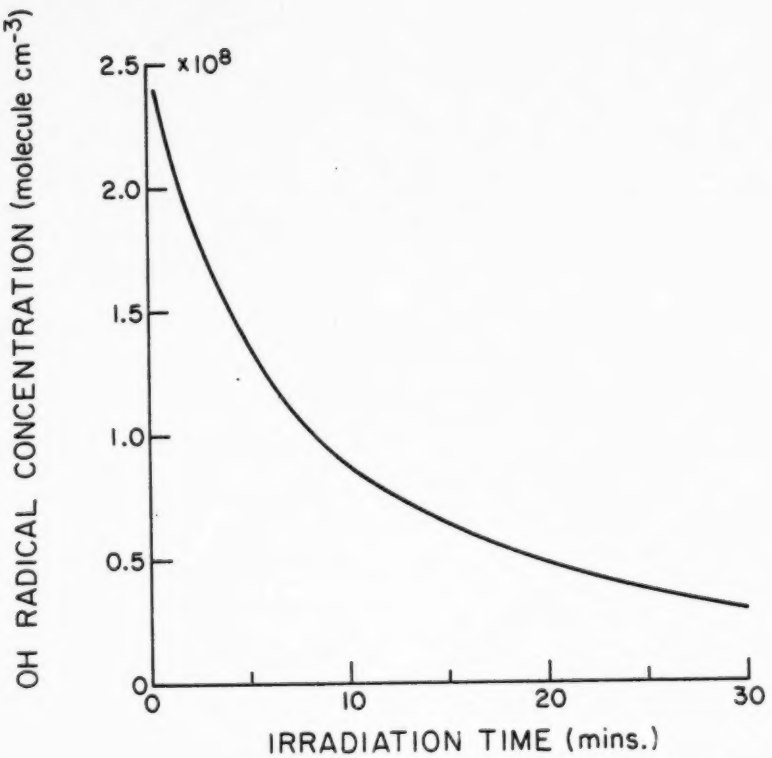


Figure 11. OH Radical Concentrations during a Typical Irradiation at Full Light Intensity with an Initial Concentration of CH_3ONO of 10 ppm

three irradiations should be carried out, with CH_3ONO concentrations of 0, ~5 ppm and ~15 ppm. For organics which do not photolyze at least two irradiations should be carried out with CH_3ONO concentrations of ~5 and ~10 ppm.

It is also recommended that two of the reference organics be tested against one another periodically, as a check on the experimental system (e.g., irradiations of CH_3ONO/NO/n-butane/cyclohexane/air mixtures).

E. Data Analysis

The concentrations of the test compound and reference organic, as analyzed by gas chromatography, are used to plot equation (IX). From the plot of equation (IX), as shown in Figure 12 for irradiations of a series of ketones and cyclohexane, a least squares analysis of the slope yields the rate constant ratios k_1/k_2.

F. Reference Organics

These organics are chosen for ease of gas chromatographic analyses and must have accurately known OH radical rate constants. Preferably, they should not react with O_3, nor should they photolyze. Also, their OH radical rate constant should be similar, preferably to within a factor of two to three, to that for the test compound. Table 3 gives a list of recommended reference organics, together with their OH radical and O_3 reaction rate constants at room temperature.

G. Information to be Reported

A report of the results should include for each test compound the following:

a. The compound's name, formula and physical properties (boiling and melting points)
b. The chemical's physical form used during injection (gas or liquid at room temperature), method of purification and purity (including analysis of impurities)
c. The temperature during each run
d. The name and formula of the reference organic used and the rate constant k_2 used in the data analysis

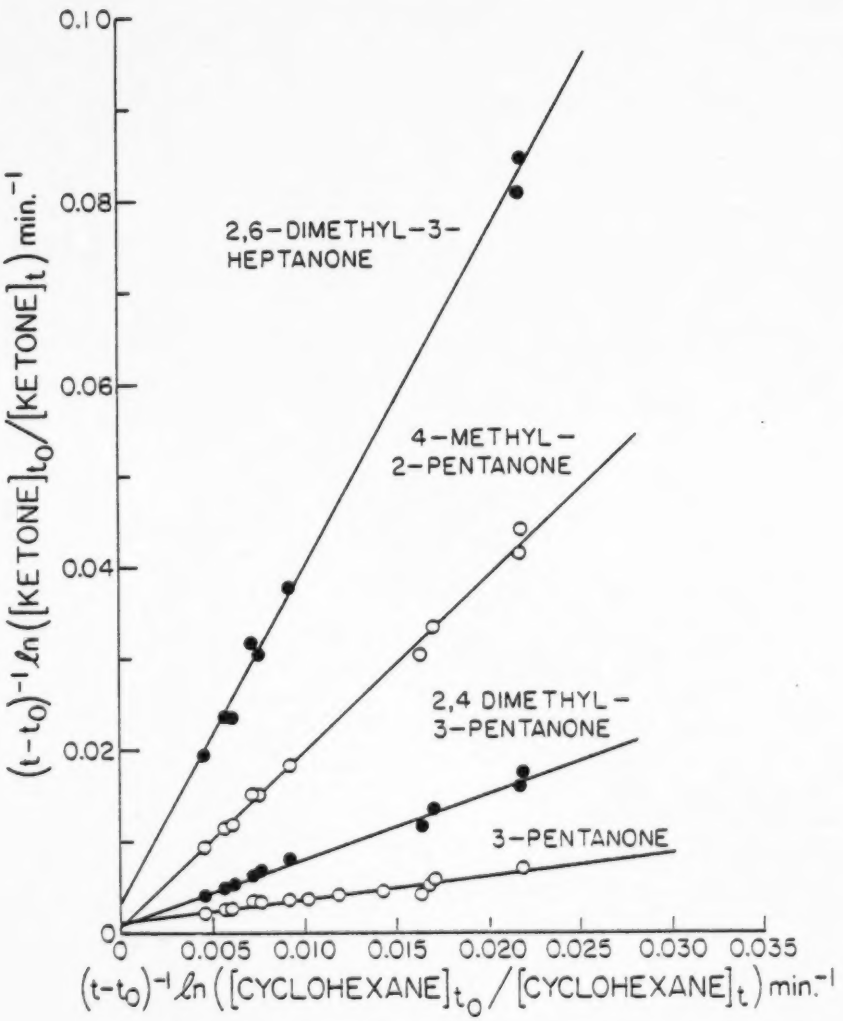


Figure 12. Plot of Equation (IX) for a Series of Ketones, using Cyclohexane as the Reactant Organic

Table 3. List of Reference Organics for which Accurate OH Radical and O_3 Reaction Rate Constants are Available, and which do not Photolyze

Organic	$10^{12} \times k^{OH}$ (cm^3 $molecule^{-1}sec^{-1}$)[a]	$10^{18} \times k^{O_3}$ (cm^3 $molecule^{-1}sec^{-1}$)[a]
n-Butane	2.6[c]	b
Cyclohexane	7.6[c]	b
Ethene	8.5[c]	1.6[d]
Propene	25[c]	12[d]
Isoprene	96[c]	12[e]
2-Methyl-2-butene	87[c]	445[f]

[a]At 298 K.
[b]Negligible.
[c]Atkinson et al. (1982a) and references therein.
[d]Atkinson et al. (1982b) and references therein.
[e]Atkinson et al. (1982c).
[f]Mean of data from Japar et al. (1974) and Huie and Herron (1975).

e. The initial concentrations of the reference organics and test compound, NO and CH_3ONO
f. The data obtained (i.e., the concentrations of the reference organic and test compound prior to and during irradiation, and the values of $(t-t_o)^{-1}$ ln ([reference organic]$_{t_o}$/[reference organic]$_t$) and $(t-t_o)^{-1}$ ln ([test compound]$_{t_o}$/[test compound]$_t$).
g. Plots of equation (IX) and, if the test compound does not photolyse, equation (X)
h. The value of k_1/k_2 and hence of k_1 determined by least squares analysis from such a plot
i. Calculated 1/e lifetime for 1×10^6 molecule cm^{-3} of OH radicals.

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